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## (54) PRODUCTION OF (METH)ACRYLIC POLYMER HAVING TERMINAL FUNCTIONAL GROUP

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a process for producing a (meth)acrylic polymer having a large amount of terminal crosslinkable functional groups such as alkenyl or crosslinkable silyl groups and to provide a curable composition comprising the same.

**SOLUTION:** An initiator comprising an organic halide or halogenated sulfonyl compound and a catalyst comprising a metal complex having as the central metal an element belonging to Group 8, 9, 10, or 11 or the Periodic Table are used for polymerization to obtain a (meth)acrylic polymer having a terminal structure represented by the formula  $-CH_2-C(R_1)(CO_2R_2)(X)$  ( $R_1$  is hydrogen or methyl;  $R_2$  is a 1-20C alkyl, aryl, or aralkyl; and  $X$  is chloride, bromine, or iodine). The halogen atoms of the polymer are replaced with substituents each having an alkenyl or crosslinkable silyl group to obtain the target polymer.

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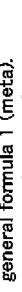
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## CLAIMS

## [Claim(s)]

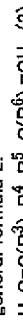
[Claim 1]An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table. Are obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. A manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta) changing into an alkenyl group content substituent halogen of an acrylic polymer which has terminal structures shown by the general formula 1 (meta).



(As for hydrogen or a methyl group, and R<sup>1</sup>, in inside of formula, and R<sup>2</sup>, an alkyl group of 1~20, an aryl group or an aralkyl group, and X are [ a carbon number ] chlorine, bromine, or iodine)

[Claim 2]An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table. An acrylic polymer which has terminal structures which show nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. The manufacturing method according to claim 1 making a compound having an alkenyl group of polymerization nature, and other at least one alkenyl group react.

[Claim 3]The manufacturing method according to claim 2 which is a compound in which a compound having an alkenyl group of polymerization nature and other at least one alkenyl group is shown by the general formula 2.



(As for R<sup>3</sup> and R<sup>6</sup>, -C(O) O- (ester group) or o-, m-, p-phenylene group, and R<sup>5</sup>, may include one or more ether bonds among a formula by a divalent organic group of direct coupling or the carbon general formula 2.

[Claim 4]The manufacturing method according to claim 1 making an organic metallic compound which has an alkenyl group react to an acrylic polymer which has terminal structures shown by the general formula 1 (meta).

[Claim 5]The manufacturing method according to claim 4, wherein an organic metallic compound H<sub>2</sub>C=C(R<sup>7</sup>)C(R<sup>8</sup>)(R<sup>9</sup>)Sn(R<sup>10</sup>)<sub>3</sub> (3)

which has an alkenyl group is an organic tin compound shown by the general formula 3.

[Claim 6]The manufacturing method according to claim 5, wherein an organic halogenated among a formula, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup> may be mutually the same at hydrogen or an alkyl group of the carbon numbers 1~10, an aryl group, or an aralkyl group, or may differ from each other. R<sup>10</sup> is an alkyl group of the carbon numbers 1~10, an aryl group, or an aralkyl group.

[Claim 7]The manufacturing method according to claim 6, wherein an organic halogenated compound which is an initiator, or a sulfonyl halide compound is a halogenide which has an alkenyl group.

[Claim 8]The manufacturing method according to claim 6 which is a compound in which a halogenide which has an alkenyl group is shown by the general formula 4 or 5.



inside of formula, and R<sup>1</sup> — hydrogen or a methyl group, R<sup>11</sup>, and R<sup>12</sup> — hydrogen. Or a univalent alkyl group of the carbon numbers 1~20, an aryl group, an aralkyl group or a thing mutually connected

in the other end, and R<sup>3</sup>, -X in which C(O) O- (ester group), -C(O)- (keto group) or o-, m-, p-phenylene group, and R<sup>14</sup> may include one or more ether bonds by a divalent organic group of direct coupling or the carbon numbers 1~20 is chlorine, bromine, or iodine.



(a formula — inside — R — — one ... — R — — 11 — — R — — 12 — — R — — 14 — — X — the above — the same — R — — 15 — — direct coupling — C — (— O —) — O — (ester group) — Cl(O) — (ketone group) or o-, m-, and p-phenylene group)

[Claim 8]An acrylic polymer which has the structure which is shown to one end by alkenyl group and shown in other ends by the general formula 1 by a method of claim 6 or 7 (meta) is manufactured, A manufacturing method of an acrylic polymer which has an alkenyl group at the end (meta) characterized by carrying out coupling of the halogen ends using a compound which can furthermore replace halogen of the general formula 1, and which has a total of two or more same or different functional groups.

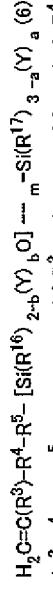
[Claim 9]The manufacturing method according to claim 8 performing a coupling reaction of the halogen ends of the general formula 1 using a compound chosen from a group which consists of polyol, polyamine, polycarboxylic acid, polythiol and those salts, and an alkaline metal sulfide. [Claim 10]A) an acrylic polymer which has an alkenyl group at the end obtained by one method of claims 1~9 (meta), and a hardenability constituent containing (B) hydroxyl group content compound.

[Claim 11]A) The hardenability constituent according to claim 10 which has a molecular weight of an acrylic polymer which has an alkenyl group at the end of an ingredient (meta) in the range of 50~50000.

[Claim 12]An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table. Are obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) changing into a crosslinkable=silyl-groups content substituent halogen of an acrylic polymer which has terminal structures shown by the general formula 1 (meta).

[Claim 13]An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table. An acrylic polymer in which nine fellows, ten fellows, or 11 group elements are shown by the general formula 1 (meta) used as a central metal as a catalyst (meta) is manufactured. The manufacturing method according to claim 12 making a compound having an alkenyl group and crosslinkable silyl groups of polymerization nature react.

[Claim 14]The manufacturing method according to claim 13 whose compound having an alkenyl group and crosslinkable silyl groups of polymerization nature is a compound shown by the general formula 6.



{R<sup>3</sup>, R<sup>4</sup>, and R<sup>5</sup> among a formula} R<sup>3</sup> in the general formula 2, R<sup>4</sup>, and R<sup>5</sup> — the same — R<sup>16</sup> and R<sup>17</sup>. All An alkyl group of the carbon numbers 1~20, an aryl group, an aralkyl group. Or (R')<sup>3</sup> SiO — (R' is a univalent hydrocarbon group of the carbon numbers 1~20, and) three R' being the same and differing — \*\*\* — when the Tori ORGANO siloxy group shown is shown and R<sup>16</sup> or two or more R<sup>17</sup> exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolytic basis and two or more Y exists, they may differ. When Y shows 0, 1, 2, or 3, and b shows 0, 1, or 2, m is an integer of 0~19. However, it shall satisfy that it is a+m>b≥1.

[Claim 15]The manufacturing method according to claim 12 to 14 which is an organic halogenated compound which is an initiator, or a halogenide in which a sulfonyl halide compound has crosslinkable silyl groups.

[Claim 16]The manufacturing method according to claim 15 which is a compound in which an organic halogenated compound which has crosslinkable silyl groups is shown by the general formula 7 or 8. R<sup>11</sup>R<sup>12</sup>C(X)-R — 13-R<sup>14</sup>-C(H)(R<sup>1</sup>) CH<sub>2</sub>-[Si(R'16) 2-b(Y) ]<sub>b</sub>O ]<sub>m</sub>-Si[R'17) 3-a(Y) <sub>a</sub>  
(The inside of a formula, R<sup>1</sup>, R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup>, R<sup>14</sup>, R<sup>16</sup>, R<sup>17</sup>, a, b, m, X, and Y are the same as the above)

(R<sup>17</sup>)<sub>3-a</sub> {Y} Si-[OS(R<sup>16</sup>)<sub>2-b</sub>(Y)'<sub>b</sub>] <sup>m</sup>-CH<sub>2</sub>-C(H)(R<sup>1</sup>)-R<sup>14</sup>-C(R<sup>11</sup>)(X)-R<sup>15</sup>-R<sup>12</sup> (8)

(The inside of a formula, R<sup>1</sup>, R<sup>11</sup>, R<sup>12</sup>, R<sup>14</sup>, R<sup>15</sup>, R<sup>16</sup>, R<sup>17</sup>, a, b, m, X, and Y are the same as the above)

[Claim 17] An acrylic polymer which has the structure which is shown to one end by crosslinkable silyl groups, and is shown in other ends by the general formula 1 by a method of claim 15 or 16 (meta) is manufactured. A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) characterized by carrying out coupling of the halogen ends using a compound which can furthermore replace halogen of the general formula 1, and which has a total of two or more same or different functional groups.

[Claim 18] The manufacturing method according to claim 17 performing a coupling reaction of the halogen ends of the general formula 1 using a compound chosen from a group which consists of polyol, polyamine, polycarboxylic acid, polythiol and those salts, and an alkaline metal sulfide.

[Claim 19] A manufacturing method of an acrylic polymer which has crosslinkable silyl groups at the end (meta) making hydrosilane which has crosslinkable silyl groups add to an acrylic polymer which has an alketyl group at the end obtained by one method of claims 1-9 (meta).

[Claim 20] A hardenability constituent which uses as the main ingredients an acrylic polymer which is obtained by one of methods according to claim 12 to 19, and which has crosslinkable silyl groups at the end (meta).

[Claim 21] The hardenability constituent according to claim 20 which has a molecular weight of an acrylic polymer which has crosslinkable silyl groups at the end (meta) in the range of 500-50000.

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## DETAILED DESCRIPTION

### Detailed Description of the Invention

[0001] [Field of the Invention] This invention relates to the hardenability constituent which used for the end

the manufacturing method of a functional group and the acrylic polymer which specifically has an alkenny group or crosslinkable silyl groups (meta), and this polymer.

[0002] [Description of the Prior Art] The polymer which has a functional group at the end constructs a bridge

by combining with a the very thing independent or a suitable hardening agent, and giving the hardened material which was excellent in heat resistance, endurance, etc. is known. The polymers which have an alkenny group or crosslinkable silyl groups at the end especially are those examples of representation. The polymer which has an alkenny group at the end carries out bridge construction

hardening using a hydrosilyl group content compound as a hardening agent, or by using the photoreaction. The polymer which has crosslinkable silyl groups at the end gives a hardened material by absorbing hygroscopic surface moisture under existence of a suitable condensation catalyst.

[0003] As a principal chain skeleton of the polymer which it has at the end, such an alkenny group or crosslinkable silyl groups, Polyether system polymers, such as polyethylene oxide, polypropylene oxide, polytetramethylene oxide, Hydrocarbon system polymers, such as polybutadiene, polyisoprene, polychloroprene, polyisobutylenes, or those hydrogenation things, Polyester system polymers, such as polyethylenglycine terephthalate, polybutylene terephthalate, and polycaprolactone, etc. are illustrated, and it is used for various uses based on a principal chain skeleton and bridge construction form.

[0004] [Problem(s) to be Solved by the Invention] What has a functional group at the end with the polymer of a vinyl system obtained by a radical polymerization by one side of the polymer which was illustrated above, and which is obtained by ionic polymerization or condensation polymerization has hardly been put in practical use yet. Also in a vinyl system polymer, an acrylic (meta) polymer, It has the characteristics which are not obtained in an above-mentioned polyether system polymer,

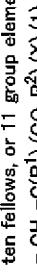
hydrocarbon system polymer, or polyester system polymer, such as high weatherability and transparency, what has an alkenny group and crosslinkable silyl groups in a side chain is used for the high weatherability paint etc.

[0005] If the acrylic polymer which has an alkenny group or crosslinkable silyl groups in molecular chain terminals (meta) can be obtained by a simple method, the hardened material which excelled [side chain] in hardened material physical properties as compared with what has a cross-linking group can be obtained. Therefore, although the manufacturing method has been examined by the researcher of the former many, it is not easy to manufacture them industrially.

[0006] Use alkenny group content disulfide for JP,5-255415,A as a chain transfer agent. The synthetic method of the acrylic polymer which has an alkenny group in both ends (meta) again to JP,5-262808,A. Although the acrylic polymer which has hydroxy in both ends (meta) is compounded using the disulfide which has hydroxyl and the synthetic method of the acrylic polymer which has an alkenny group in both ends further using the reactivity of hydroxyl (meta) is indicated, It is not easy to introduce an alkenny group into both ends certainly by these methods. On the other hand to JP,59-16014,A, the manufacturing method of the acrylic polymer which has crosslinkable silyl groups as a chain transfer agent in the both ends using the disulfide compound which has crosslinkable silyl groups (meta). Although the manufacturing method of the acrylic polymer which has crosslinkable silyl

groups in both ends (meta) by using for JP,61-133201,A the hydrosilane which has crosslinkable silyl groups, and halogenation Silang is indicated. In these methods, it is difficult to introduce crosslinkable silyl groups into both ends certainly, and the hardened material which has the satisfactory characteristic cannot be obtained. In order to introduce a functional group into an end certainly, a chain transfer agent must be used in large quantities, and it is a manufacturing process top problem. [0007] Therefore, let it be SUBJECT to provide the manufacturing method of the acrylic polymer which has an alkenny group or crosslinkable silyl groups by a high ratio at the end as compared with the conventional method (meta), and the hardenability constituent using them in this invention.

[0008] [Means for Solving the Problem] An acrylic polymer which has an alkenny group at the end among aforementioned problems (meta), An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, It is obtained by changing into an alkenny group content substituent halogen of an acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst.



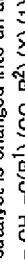
(As for hydrogen or a methyl group, and R<sup>2</sup>, in inside of formula, and R<sup>1</sup>, an alkyl group of 1~20, an aryl group or an aralkyl group, and X are [ a carbon number ] chlorine, bromine, or iodine.) As an example of such a manufacturing method, an organic halogenated compound or a sulfonyl halide compound An initiator, An acrylic polymer which has the structure which shows the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. A method of making an organic metallic compound which has an alkenny group react to an acrylic polymer which has a method to which a compound having an alkenny group of polymerization nature and other at least one alkenny group is made to react, or terminal structures shown by the general formula 1 (meta), etc. are mentioned. A halogenide which has an alkenny group, or a sulfonyl halide compound is used as an initiator. An acrylic polymer which has an alkenny group in one end and has the structure of the formula 1 at other ends (meta), and changing halogen of the end into an alkenny group content substituent.

[0009] An acrylic polymer which is obtained by such a method and which has an alkenny group at the end (meta) is used for an acrylic polymer which has an alkenny group at the (A) end (meta), and a hardenability constituent containing (B) hydrosilyl group content compound. An acrylic polymer which has crosslinkable silyl groups at the end (meta). An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, It can manufacture by changing into a crosslinkable-silyl-groups content substituent halogen of an acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst. As an example of such a manufacturing method, an organic halogenated compound or a sulfonyl halide compound An initiator, An acrylic polymer which has terminal structures which show the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements by the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. A method to which a compound having an alkenny group and crosslinkable silyl groups of polymerization nature is made to react is mentioned. A halogenide which has crosslinkable silyl groups is used as an initiator, It can obtain also by manufacturing an acrylic polymer which has crosslinkable silyl groups in one end, and has the structure shown in other ends by the formula 1 (meta), and changing halogen of the end into a crosslinkable-silyl-groups content substituent further.

[0010] An acrylic polymer which has crosslinkable silyl groups at the end (meta) can be manufactured also by making hydrosilane which has crosslinkable silyl groups add to an acrylic polymer which has an alkenny group at the end (meta). Thus, an acrylic polymer which has crosslinkable silyl groups at the end obtained (meta) can be used as a hardenability constituent.

[0011] It also has the feature that an acrylic polymer which has a functional group of cross-linking at the end obtained by this invention (meta) has narrow molecular weight distribution.

[Embodyment of the Invention] First, the manufacturing method of the acrylic polymer which has an alkene group at the end (meta), An organic halogenated compound or a sulfonyl halide compound And initiator, the 8th fellows of the periodic table, The halogen of the acrylic polymer which has terminal structures which show by the general formula 1 (meta) obtained by the polymerization method using the metal complex which uses an alkene, ten fellows, ten fellows, or 11 group elements as a central metal as a catalyst is changed into an alkene group content substituent



(As for hydrogen or a methyl group, and  $R^2$ , in inside of formula, and  $R^1$ , the alkyl group of 1-20, an aryl group or an aralkyl group, and X are [ a carbon number ] chlorine, bromine, iodine), The method of using a carbon tetrachloride, carbon tetrabromide, a methylene chloride, a methylene bromide, etc. for an end in the polymerization which uses a halogenide as a chain transfer agent (TEROGEN) as a manufacturing method of the acrylic polymer which has halogen (meta) is used. However, it is difficult to introduce halogen into both ends certainly by this method. [0013] If the living radical polymerization studied energetically these days is used to this method, halogen is introduced into an end by a high ratio (Matyjaszewski et al. [ for example, 1]. J. Refer to Am. Chem. Soc. 99: 117 and 5614, Macromolecules 1995, 28, and 7901, Science 1996, 272, and 868 c, Sawamoto et al., and Macromolecules 1995, 28, and 1721. Though these methods are radical polymerizations, a polymerization advances in living, the narrow ( $M_w/M_n=1.1-1.5$ ) polymer of molecular weight distribution is obtained, and a molecular weight can be freely controlled by the nreneportion ratio of a monomer and an initiator.

[0014] The organic halogenated compound which has an organic halogenated compound and a carbon halogen bond with especially high reactivity in this living radical polymerization. (For example, the ester compound which has halogen in an alpha position and the compound which has halogen in a benzyl position), or a sulfonyl halide compound is used as an initiator. As a catalyst, the metal complex which uses the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 Group elements as a central metal is used. As a metal kind, univalent copper, a divalent ruthenium, and divalent iron are especially preferred. If it illustrates concretely, they will be a cuprous chloride, the first copper of bromination, a cuprous iodide, a cuprous cyanide, copper I oxide, the first copper of acetic acid, the first copper of perchloric acid, etc. When using a copper compound, in order to improve catalytic activity, ligands, such as a 2,2'-bipyridyl and its derivative, a 1,10-pheanthroline, and its derivative, are added. The triphenyl phosphine complex ( $RuCl_2(PPh_3)_3$ ) of ruthenium chloride of bivalence is also preferred as a catalyst. when using this catalyst, in order to improve the activity --- doria --- aluminum compounds, such as RUKOKI sial minium, are added. The triphenyl

[0015] In order to obtain the acrylo (meta) polymer of cross-linking using this polymerizing method, the organic halogenated compound which has the two or more starting points, or a sulfonyl halide compound is used as an initiator. If it illustrates concretely,  $\text{o}^-, \text{m}^-, \text{p}^-$ - $\text{XCH}_2\text{-C}_6\text{H}_4\text{-OH}_2\text{X}$ ,  $\text{o}^-, \text{m}^-, \text{p}^-$ - $\text{CH}_3\text{C}(\text{H})\text{-C}_6\text{H}_4\text{-C}(\text{H})(\text{XOCH}_3)\text{-C}_6\text{H}_4\text{-C}(\text{X})(\text{CH}_3)^2$  (however, inside of upper chemical formula, and  $\text{C}_6\text{H}_4$  a phenylene group and X chlorine, bromine, or iodine),  $\text{RO}_2\text{C-C}(\text{H})(\text{X})\text{-}\left(\text{CH}_2\right)_n\text{-C}(\text{H})(\text{X})\text{-CO}_2\text{R}$ ,  $\text{RO}_2\text{C-C}(\text{H})(\text{X})\text{-}\left(\text{CH}_2\right)_n\text{-C}(\text{H})(\text{X})\text{-CO}_2\text{R}$ ,  $\text{RC(O)-CH}_2\text{-C}(\text{H})(\text{X})\text{-}\left(\text{CH}_2\right)_n\text{-C}(\text{H})(\text{X})\text{-CO}_2\text{R}$ ,  $\text{RC(O)-CH}_2\text{-C}(\text{H})(\text{X})\text{-}\left(\text{CH}_2\right)_n\text{-C}(\text{H})(\text{X})\text{-CO}_2\text{R}$  (as for the alkyl group of the carbon numbers 1-20, an aryl group or an aralkyl group, and n, in the inside of a formula, and the integer of 0-20 and X are chlorine, bromine, or iodine),  $\text{XCH}_2\text{C(O-CH}_2\text{X)}\text{ and } \text{CH}_3\text{C(H)(X)-CH}_3$ ,  $\text{(CH}_3\text{)}_2\text{C(X)(CH}_3\text{)}_2\text{C(O-CH}_2\text{X)}\text{ and } \text{C}_6\text{H}_5\text{C(H)}$  $\text{-C}(\text{H})(\text{X})\text{-CH}_2\text{-C(H)(X)-CH}_3$  (as for the inside of the inner formula and X chlorine, bromine, or iodine).

and n are the integers of (0-20),  
 $XCH_2CO_2(CH_2)_n - COOCH_2X$ ,  $CH_3O(H) COCO_2-(CH_2)_n - OCCO(H) X$ ,  $(CH_3)_2C(X)CO_2-(CH_2)_n$   
 $OCCO(X)(CH_3)_2$  (as for the inside of the upper formula, and X, chlorine, bromine, iodine, and n are  
the integers of (0-20),  
 $XCH_2CO(H) COO(CH_2)_n - COOCH_2X$  and  $CH_3O(H) COCO_2-(CH_2)_n - OCCO(H) X$ ,  
 $C(X)COO(CH_2)_n - COOCH_2X$

2- $\sigma$ -, m-, p-XCH<sub>2</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-OCOCH<sub>2</sub>X, o-, m-, p-CH<sub>3</sub>CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-COC(X)CH<sub>3</sub>, o-, m-, p-(CH<sub>3</sub>)<sub>2</sub>C(X)CO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-OCOC(X)CH<sub>3</sub>, 2-, o-, m-, p-XSO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub>X (the inside of the upper formula and X are chlorine, bromine, or iodine).

\*\*\* is mentioned.

[0016] As an acrylic monomer used in this polymerization (meta), there are no restrictions in particular and various kinds of things can be used. If it illustrates, methyl acrylate (meta), ethyl acrylate (meta), (Meta) Acrylic acid-*n*-propyl, acrylic acid (meta) isopropyl, (Meta) Acrylic acid-*n*-butyl, isobutyl acrylate (meta), (Meta) Acrylic acid-tert-butyl, acrylic acid (meta)-*n*-pentyl, (Meta) Acrylic acid-*n*-hexyl, acrylic acid (meta) cyclohexyl, (Meta) Acrylic acid-*n*-heptyl, acrylic acid (meta)-*n*-octyl, (Meta) Acrylic acid-2-ethylhexyl, acrylic acid (meta) nonyl, (Meta) Decyl acrylate, acrylic acid (meta) dodecyl, acrylic acid (meta) phenyl, (Meta) They are acrylic acid toluyl, acrylic acid (meta) benzyl, acrylic acid (meta)-2-methoxy ethyl, acrylic acid (meta)-3-methoxy butyl, acrylic acid (meta)-2-hydroxyethyl, acrylic acid (meta)-2-hydroxypropyl, etc. Even if it uses these independently and they mix and use two or more sorts, they are not cared about. Carrying out copolymerization of other vinyl system monomers, such as styrene, alpha-methylstyrene, acrylonitrile, if needed does not interfere at all.

[0017] A polymerization can be performed in a non-solvent or various kinds of solvents. A polymerization can be performed in room temperature -200 °K, and it is 50-150 °K preferably. The acrylic polymer which has an alkkenyl group at the end (meta) can be obtained by changing halogen of the acrylic polymer which is obtained by the above-mentioned polymerization and which has halogen

[0018] As such a method, first, the acrylic polymer which has terminal structures shown by the general formula 1 by the above-mentioned polymerization (meta) is manufactured, and the method to which the compound it has a compound and an alkene group of polymerization nature and other at least one alkene group further is made to react as the 2nd monomer is mentioned. In the above-mentioned polymerization, the polymerization end holds polymerization activity, and if a vinyl system monomer is newly added, a polymerization will advance again. Therefore, if the vinyl system monomer having the alkene group of polymerization nature and other at least one alkene group is added, A radical addition reaction occurs in a polymerization activity alkene<sup>†</sup> group portion, other alkene groups remain, while it has been unreacted, and the acrylic polymer which has an alkene group at the end (meta) is obtained. After the 1st polymerization is completed and it isolates a polymer, it may add with a catalyst and such 2nd monomer may be made to newly react, and it may add in the middle of a polymerization (in-situ), and it may be made to react. In the case of the latter, the monomer inversion rate of the 1st polymerization is so good that it is high, and is not less than 80% preferably. An alkene group will be distributed over the side chain instead of a molecular terminal as it is 80% or less, and the mechanical characteristic of a hardened material will be spoiled.

[0019] Under the present circumstances, the compound having the alkene group of such polymerization nature, and other at least one alkene group, if a quantity equal to the number of polymerization ends (it is almost equal to the number of the starting points of an initiator since it is living polymerization) is added, one alkene group will be theoretically introduced into all the ends at a time, but, in order to introduce an alkene group into a whole end certainly, specifically, it is good to use one to 5 times to the number of ends in excessive amount. If it uses more mostly than 5 times, an alkene group will be introduced into the end of a polymer by high density, and it is not desirable on hardened material physical properties.

[0020] Although there is no restriction in particular as a compound having the alkene group of polymerization nature, and other at least one alkene group, it is general formula  $2H_2C=O(R^3)-R^4-R^5-C(R^6)=CH(2)$ , for example,

the inside of a formula,  $R^3$ , and  $R^6$  — hydrogen or methyl, and  $R^4$ —C(O)O— (ester group). Or  $\sigma$ -,  $m$ -,  $p$ -phenylene group, and  $R^5$  may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1-20. The compound shown is mentioned. As for the thing of an ester group,  $R^4$  is [an acrylate (meta) system compound and  $R^4$  of the thing of a phenylene group] the compounds of a styrene system. As  $R^5$  in the general formula 2, alkylene groups, such as methylene, ethylene, propylene, and so on, and various other bonds such as aryl, crown compounds, and so on, and so on.

such as o-, m-, p-phenylene group, and benzyl, ] and  $\text{CH}_2\text{CH}_2\text{-O-CH}_2\text{-}$  and  $\text{-O-CH}_2\text{-}$ , are

[0026] Various kinds of things can be used as an electrophilicity compound which has an alkenyl group. For example, they are an alkenyl group content compound which has a leaving group like halogen or an acetyl group, a carbonyl compound which has an alkenyl group, an isocyanate compound which has an alkenyl group, the acid halide which has an alkenyl group, etc. If the alkenyl group content compound which has a leaving group like halogen or an acetyl group among these is used, since a hetero atom will not be introduced into a main chain and the weatherability which is the original feature of an acrylic (meta) polymer will not be lost, it is desirable.

[0027] Also in such a leaving group content alkenyl compound, for the reason reactivity is high,

such as o-, m-, p-phenylene group, and benzyl, ] and  $-CH_2CH_2-O-CH_2-$  and  $-O-CH_2-$ , are illustrated.

[0021] H from the point that acquisition is easy also in these  $\text{---}_2=C\text{C}[(\text{H})](\text{O})\text{O}(\text{CH}_2)_n-\text{CH=CH}_2$  and  $\text{H} \longrightarrow \text{---}_2=\text{O}(\text{CH}_3)\text{C}(\text{O})(\text{OH}_2)_n-\text{CH=CH}_2$  (in each of above-mentioned formulas, n is an integer of 0~20),  $\text{H}_2\text{O}=\text{C}(\text{H})\text{O}(\text{O})(\text{OH}_2)_n-\text{O}-(\text{CH}_2)_m\text{CH=CH}_2$ ,  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m\text{CH=CH}_2$  (in each of above-mentioned formulas, n is an integer of 1~20 and m is an integer of 0~20),

\*\* — it is desirable.

[0022] If it is considered as the method of introducing an alkenyl group into an end, various kinds of organic metallic compounds which have an alkenyl group can be made to be able to act on the end shown by the formula 1 to the polymer which has halogen, and the method of replacing halogen directly can also be used. As such an organic metallic compound, organic lithium, organic sodium, organic potassium, organic magnesium, organic zinc, organic copper, etc. are mentioned. Organic tin and an organocopper compound are preferred at the point that react especially to halogen of the formula 1 selectively, and reactivity with a carbonyl group is low.

[0023] As an organic tin compound which has an alkenyl group, although there is no restriction in particular, the compound shown by the general formula 3 is preferred.

$$\text{H}_2\text{C}=\text{C}(\text{R}^7)\text{C}(\text{R}^8)(\text{R}^9)\text{Sn}(\text{R}^{10})_3 \quad (3)$$

among the formula,  $\text{R}^7$ ,  $\text{R}^8$ , and  $\text{R}^9$  may be mutually the same or hydrogen or the alkyl group of the carbon numbers 1-10, an aryl group, or an aralkyl group, or may differ from each other.  $\text{R}^{10}$  is an alkyl group of the carbon numbers 1-10, an aryl group, or an aralkyl group.

If the example of the organic tin compound of the formula 3 is shown, allyl tributyl tin, allyl trimethyl tin, ant RUTTOR (n-octyl) tin, ant RUTTOR (cyclohexyl) tin, etc. will be illustrated. The alkenyl group content organic tin compound shown by the general formula 3. It may add in the middle of the polymerization of an acrylic system monomer (meta), and the acrylic polymer which has terminal structures of the general formula 1 (meta) may be made to react anew, since it reacts to end halogen advances only with heating, but in order to promote a reaction, radical initiators, such as azobisisobutyronitrile, may be added.

[0024] As an organocopper compound which has an alk enyl group, diaryl copper lithium, diaryl copper lithium, diisopropenyl copper lithium, etc. are illustrated. As a converting method to the alk enyl group of an end halogen group, it is also possible to use the method of making it react to the electrophilicity compound which makes a metal simple substance or an organic metallic compound act, metal-izes halogen to the acrylic polymer which has halogen at the end (meta), and has an alk enyl group after an appropriate time.

[0025] As a metal simple substance, alkaline-earth metals, such as lithium, sodium, and potassium, magnesium, and calcium, aluminum, zinc, etc. are mentioned. The point that a side reaction which the metal-ized portion (eno rate anion) attacks other ester groups among these, or it transfers does not occur easily to especially zinc is preferred. As an example of an organic metallic compound, organic magnesium, such as organic lithium, organic sodium, organic potassium, and a Grignard reacting agent, organic aluminium, an organozinc compound, etc. are mentioned. In order to make halogen metal-ize efficiently, it is preferred to use organic lithium and organic

[0026] Various kinds of things can be used as an electrophilicity compound which has an alkenyl group. For example, they are an alkenyl group content compound which has a leaving group like halogen or an acetyl group, a carbonyl compound which has an alkenyl group, an isocyanate compound which has an alkenyl group, the acid halide which has an alkenyl group, etc. If the alkenyl group content compound which has a leaving group like halogen or an acetyl group among these is used, since a hetero atom will not be introduced into a main chain and the weatherability which is the original feature of an acrylic (meta) polymer will not be lost, it is desirable.

[0027] Also in such a leaving group content alkenyl compound, for the reason reactivity is high. VCM/PVC, vinyl bromide, iodination vinyl, isopropenyl chloride, isopropenyl bromide, iodination isopropenyl, an allyl chloride, an allyl bromide, allyl iodide, a 3-chloro-1-butene, A 3-bromo-1-butene a 3-iodo-1-butene, a 3-chloro-2-methyl-1-propene, A 3-bromo-2-methyl-1-propene, a 3-iodo-2-methyl-1-propene, Allyl acetate, a 3-acetoxy-1-butene, a 3-acetoxy-2-methyl-1-propene, Chloride-4-vinylbenzyl and 4-allylbenzyl chloride, bromination-4-vinylbenzyl, and 4-allylbenzyl bromide is preferred, and an allyl chloride, an allyl bromide, allyl iodide, and especially allyl acetate are preferred at the point that acquisition is still easier.

[0028] To halogen of the end of the formula 1, makes a metal simple substance or an organic metallic compound act, and it metal-izes. In the manufacturing method of the acrylic polymer which has an alkenyl group at the end (meta) making an alkenyl group content electrophilicity compound react furthermore, The combination of a desirable reacting agent is using the above alkene group content compounds which have a leaving group as an electrophilicity compound, using zinc as metal. In order to advance this reaction more smoothly, various kinds of catalysts can be used, as such a catalyst – the copper compound (for example, a copper chloride,) of monovalence A copper bromide, the copper compound (for example, copper acetylacetone) of bivalence, zerovalent Ni compounds, They are (for example, tetrakis triphenyl phosphine nickelnickel(PPh<sub>3</sub>)<sub>4</sub>), zerovalent Pd compound (for example, tetrakis triphenyl phosphine palladium-d(PPh<sub>3</sub>)<sub>4</sub>), etc.

[0029] As a method of introducing an alkenyl group into an end, the end of the acrylic polymer which has halogen at the end as shown in the general formula 1 (meta) is further changed into a hydroxyl content substituent, and the method of using the reactivity of hydroxyl for after an appropriate time is mentioned. Various kinds of reactions can be used as a method of changing an end into a hydroxyl content substituent. For example, the acrylo polymer which has an end shown by the general formula 1 by the above-mentioned polymerizing method (meta) is manufactured. A method to which the compound it furthermore has a compound, and the alkenyl group and hydroxyl group of polymerization nature is made to react as the 2nd monomer. As opposed to the acrylic polymer which has a halogen end shown by the general formula 1 (meta). Make a metal simple substance or an organic metallic compound act, and halogen is metal-ized. They are the method of making it react to carbonyl compounds, such as aldehyde or ketone, the way alkali metal hydroxide like sodium hydroxide or a potassium hydrate replaces halogen directly, the way polyalcohol replaces halogen, etc.

[0030] In addition to this as a method of introducing hydroxyl into an end, the halogenide which has a hydroxyl group by polymerization using the metal complex which uses an initiator, the 8th fellows of the periodic table, nine fellows, ten Fellows, or 11 group elements as a central metal as a catalyst. The acrylic polymer which has halogen which has a hydroxyl group in one end and is shown in other ends by the formula 1 (meta). Make a metal simple substance or an organic metallic compound act, and the hydroxyl group content substituent by the method which mentioned the compound which has a total of two or more same or different functional groups that can replace these halogen further are mentioned.

[0031] Thus, as a method of introducing an alkenyl group into the acrylic polymer which has a hydroxyl group at the obtained end (meta). For example, a method on which a base like an alkenyl group content halogenide like an allyl chloride and sodium methoxide is made to act. A method on which alkenyl group content isocyanate compounds, such as an allylisocyanate, are made to act, (Meta). The method of making alkenyl group content acid halide like acrylic acid dichloride reacting under existence of bases, such as pyridine, the method of making alkenyl group content carboxylic acid like acrylic acid (meta) react under existence of a dehydration condensation catalyst, etc. are mentioned [0032] In the manufacturing method of the acrylic polymer using the metal complex which uses an initiator, the 8th fellows of the periodic table, nine fellows, ten Fellows, or 11 group elements as a

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(meta). If the organic halogenated compound which has an alkene group, or a sulfonyl halide compound is used as an initiator, the acrylic polymer which has an alkene group in an initiation terminal and in which a stop end has the structure of the formula 1 (meta) will be obtained. Thus, if halogen of the stop end of the polymer obtained is changed into an alkene content substituent, the acrylic polymer which has an alkene group in both ends (meta) can be obtained.

an enyli group, what has the structure shown in the general formula  $\pi$ , for example is illustrated.

$R^1R^{12}C(X)-R^{13}R^{14}-C(R^1)=CH_2 \quad (4)$

inside of formula, and  $R^1$  — hydrogen or a methyl group,  $R^{11}$  and  $R^{12}$  — hydrogen. Or the univalent affyl group of the carbon numbers 1-20, an aralkyl or the thing mutually connected in the other end, and  $R^{13}$ ,  $-X$  in which  $C(O)O^-$  (ester group),  $-C(O)-$  (ketone group) or  $\sigma$ ,  $m^-$ ,  $p^-$  phenylene group, and  $R^{14}$  may include one or more ether bonds by the divalent organic group of direct coupling or the carbon numbers 1-20 is chlorine, bromine, or iodine.

carbon-halogen bond is activated, and a polymerization starts these compounds.

[0034] As an example of substituent  $R^{11}$  and  $R^{12}$ , hydrogen, a methyl group, an ethyl group, a  $\pi$ -propyl group, an isopropyl group, a  $\pi$ -butyl group, a pentyl group, a hexyl group, etc. are mentioned. In the other end, may connect  $R^{11}$  and  $R^{12}$ , they may form the annular skeleton, and, in such a case,  $-R^{11}-R^{12}$  - for example,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ , etc. are illustrated.

an alkene group,  $XCH_2C(O)CC[O(CH_2)]_nCH=CH_2$  and  $CH_3CH_2C(H)_2C(O)OC(CH_2)_nCH=CH_2$ ,  $C(O)OC(CH_2)_nCH=CH_2$  and  $CH_3CH_2C(H)_2C(O)OC(CH_2)_nCH=CH_2$ ,  $[0036]$

$$\text{CO}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$$

[0037] [In each of above-mentioned formulas, as for X, chlorine, bromine or iodine, and n are the integers of 0–20)  
 $\text{XCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{CH=CH}_2$ ,  $\text{H}_3\text{CC(OH)}\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{CH=CH}_2$ ,  $(\text{H}_3\text{C})_2\text{C(X)}$  –  
 $\text{C(O)O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{CH=CH}_2$  and  $\text{CH}_3\text{CH}_2\text{C(H)}(\text{X}) - \text{C(O)O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{CH=CH}_2$ , [0038]  
[Formula 2]

$$\text{CO}_2(\text{CH}_2)_4\text{O}(\text{CH}_2)_3\text{CH}=\text{CH}_2$$

[0039] As for chlorine, bromine or iodine, and n, in X, in each of above-mentioned formulas, the integer of 1-20 and m are the integers of 0-20)  
 $\text{o,m,p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2\text{)}_n\text{-CH=CH}_2$ , o,m,p-CH<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-{(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>}, O,m,p-CH<sub>3</sub>CH(X)-C<sub>1</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub> (in each of above-mentioned formulas, as for X, chlorine, bromine or iodine, and n are the integers of 0-20)  
 $\text{o,m,p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2\text{)}_n\text{-O-(CH}_2\text{)}_m\text{-OH=CH}_2$ , o,m,p-CH<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>)<sub>m</sub>-CH=CH<sub>2</sub>, O,m,p-CH<sub>3</sub>CH<sub>2</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>)<sub>m</sub>-CH=CH<sub>2</sub> (as for chlorine, bromine or iodine, and n, in X, in each of above-mentioned formulas, an integer of 1-20 and m are the integers 0-20)  
 $\text{o,m,p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2\text{)}_n\text{-O-(CH}_2\text{)}_m\text{-O-(CH}_2\text{)}_n\text{-O-(CH}_2\text{)}_m\text{-CH=CH}_2$ , O,m,p-CH<sub>3</sub>CH<sub>2</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub> (in each of above-mentioned formulas, as for X, chlorine or iodine, and n are the integers of 0-20).

$\text{O}_{\text{m},\text{p}}-\text{X}-\text{CH}_2-\text{O}_6\text{H}_4-\text{O}-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m-\text{CH}=\text{CH}_2$ ,  $\text{O}_{\text{m},\text{p}}-\text{CH}_3\text{C}(\text{H})(\text{X})-\text{O}_6\text{H}_4-\text{O}-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m-\text{CH}=\text{CH}_2$ ,  $\text{O}_{\text{m},\text{p}}-\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})-\text{O}_6\text{H}_4-\text{O}-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m-\text{CH}=\text{CH}_2$  (as for chlorine, bromine or iodine, and n, in X, in each of above-mentioned formulas, an integer of 1-20 and m are the integers of 0-20).

A compound further shown by the general formula  $\text{b}$  as an organic halogenated compound which has an alkanyl group is mentioned.

$\text{H}_2\text{C-C(R')-R}^{14}-\text{C(R}^{11}\text{)}(\text{X})-\text{R}^{15}-\text{R}^{12}$  (5)  
 (a formula — inside — R — one — R — — 11 — R — — 12 — R — — 14 — X — the  
 above — the same — R — — 15 — — direct coupling — C — (—O—) — O — (ester group) — C(O) —  
 (ketone group) or o-, m-, and p-phenylene group are expressed)

Although  $R^{14}$  is a divalent organic group (one or more ether bonds may be included) of direct coupling or the carbon numbers 1-20, when it is direct coupling, a vinyl group has combined with carbon which has combined halogen, and it is an allyl halide ghost. In this case, since a carbon-halogen bond is activated by contiguity vinyl group there may not necessarily be any necessity of having a  $C(O)O$  basis, a phenylene group, etc. as  $R^{15}$ , and it may be direct coupling. When  $R^{14}$  is not direct coupling,

In order to activate a carbon-halogen bond, as  $R_1 - C(O) O$  basis,  $C(O)$  basis, and a phenylene group are preferred. If a compound of the formula  $\text{C}_6\text{H}_5\text{CH}_2\text{X}$  is illustrated concretely,  $\text{CH}_2=\text{CHCH}_2\text{X}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)\text{CH}_2\text{X}$ ,  $\text{CH}_2=\text{C}(\text{H})(\text{CH}_3)\text{CH}_2\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_2$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)\text{CH}_2\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_2$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHX}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_2\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHX}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_2\text{X}$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{CH}_2=\text{CHC}(\text{H})(\text{CH}_3)_3\text{X}$ .

$\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{C}(\text{H}(\text{CH}_2)_2\text{C}(\text{H}))-\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{C}(\text{H}(\text{CH}_2)_3\text{C}(\text{H}))-\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{C}(\text{H}(\text{CH}_2)_4\text{C}(\text{H}))-\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{C}(\text{H}(\text{CH}_2)_5\text{C}(\text{H}))-\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{C}(\text{H}(\text{CH}_2)_6\text{C}(\text{H}))-\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{C}(\text{H}(\text{CH}_2)_7\text{C}(\text{H}))-\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{C}(\text{H}(\text{CH}_2)_8\text{C}(\text{H}))-\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CH}(\text{CH}_2)_5\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CH}(\text{CH}_2)_6\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$  (in each of above-mentioned formulas — X — chlorine, bromine or iodine, and R —

\* can be mentioned.

(continued) An example of a suitable flame component or leaving an auxiliary gas probe is given in Figure 1.

[004] An organic halogenated compound which has an alkenyl group, or a sulfonyl halide compound It is by \*\*\*.

An initiator, if an acrylic (meta) monomer is polymerized with a polymerization method using a metal complex which uses the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal as a catalyst, it will have an alkenyl group in one end, and an acrylic polymer which has the structure shown by the formula 1 (meta) will be obtained in other ends. If a containing halogen end of the formula 1 is changed into an alketyl group content substituent, an acrylic polymer which has an alkenyl group in both ends (meta) will be obtained. It is possible to use

[0042] If an organic halogenated compound which has an alkanyl group, or a sulfonyl halide compound is used as an initiator, a polymer which is a halogen end where one end is shown by alkanyl group and other ends are shown by the formula 1 will be obtained, but An acrylic polymer which has an alkanyl group at the end (meta) can be obtained also by carrying out coupling of the halogen ends using a converting method.

compound which can replace halogen or the formula I or this polymer and which has a total of two or more same or different functional groups.

[0043] Although there is no restriction in particular as a thing which can replace end halogen shown by the formula I and which has a total of two or more same or different functional groups, polyal, polyamine, polycarboxylic acid, polythiol and those salts, an alkaline metal sulfide, etc. are preferred.]

These compounds are illustrated concretely, ethylene glycol, 1,2-propanediol, 1,3-propanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,4-butanediol, 1,2-butanediol, 2,3-butanediol, A pinacol, 1,5-pentanediol, 1,4-pentanediol, 2,4-pentanediol, 1,6-hexanediol, 1,7-heptane diol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol, 1,2-cyclopentane diol, 1,2-cyclohexane diol, 1,2-cycloheptane diol, 1,3-cyclohexanediol, 1,4-cyclohexanediol, glycerol

1,2,4-butanetriol, Catechol, resorcinol, Hydroquinone, 1,2-dihydroxynaphthalene, 1,3-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,2'-biphenol, 4,4'-biphenol, bis(4-hydroxyphenyl)methane, 4,4'-isopropylidenediphenol, 3,3'-(ethylene dioxy) diphenol, alpha and alpha'-dihydroxy-p-xylene, 1,1,1-tris(4-hydroxyphenyl) ethane, Pyrogallol, 1,2,4-benzenetriol, and alkali metal salt of the above-mentioned polyol compound. Ethylenepentane, 1,3-diaminopropane, 1,4-diaminobutane, 1,2-diamino-isobutane, 1,5-diaminopentane, 2,2-dimethyl-1,3-propanediamine, A, 1,6-hexanediamine, 1,7-heptanediamine, 1,8-octanediamine, 1,9-diaminononane, a, 1,10-diaminodecane, a 1,12-diaminododecane, 4,4'-methylenebis(cyclohexylamine), 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, 1,4-diaminocyclohexane, Alkali metal salt of 1,2-phenylenediamine, 1,3-phenylenediamine, 1,4-phenylenediamine, alpha, and alpha'-diamino-p-xylene and the above-mentioned polyamine compound, oxalic acid, malonic acid, methylmalonic acid, dimethylmalonic acid, succinic acid, glutaric acid, adipic acid, 1,7-heptane dicarboxylic acid, 1,8-octanedicarboxylic acid, 1,9-nanandedicarboxylic acid, 1,10-decane dicarboxylic acid, 1,11-undecane dicarboxylic acid, 1,12-dodecane dicarboxylic acid, 1,2-cyclopentane dicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 1,3,5-cyclohexane tricarboxylic acid, phthalic acid, isophthalic acid, Terephthalic acid, 1,2,3-benzene tricarboxylic acid, 1,2 and 4, 5-benzenetetracarboxylic acid. And alkali metal salt of the above-mentioned polycarboxylic acid, 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, 2,3-butanedithiol, 1,5-pentanedithiol, a 1,6-HEKISANJU thiol, 1,7-heptanedithiol, 1,8-octanedithiol, 1,9-nanandedithiol, 2-mercaptoproethyl ether, p-xylene alpha, alpha' - and it reaches, [JICHIORU and [1,2-benzene] [1,3-benzene] [1,4-benzene]. They are alkali metal salt of the above-mentioned polythiol compound, a lithium sulfide, a sodium sulfide, a potassium sulfide, etc. [Q044] When using the above-mentioned polyol, polyamine, polycarboxylic acid, and polythiol, In order to promote a substitution reaction, it is used together by basic compound and as the example, Lithium, sodium, potassium, sodium carbonate, potassium bicarbonate, sodium methoxide, a potassium methoxide, tert-butoxysodium, tert-butoxypotassium, sodium methide, a potassium methide, etc. are mentioned

[0045] The acrylic polymer which is obtained by various kinds of above-mentioned methods and which has an alkene group at the end (meta) can make this a hardenability constituent used as base resin. This hardenability constituent is an acrylic polymer which is obtained by one method of the (A) above and which has an alkene group at the end (meta), and a hardenability constituent containing (B)

[0046] (A) An acrylic polymer which has an alk enyl group at the end of an ingredient (meta) may be used independently, or two or more kinds may be mixed and it may be used. (A) Although there is no restriction in particular as a molecular weight of an ingredient, it is preferred that it is in the range of 500-50000. The original characteristic of an acrylic (meta) polymer it is hard to be revealed to be 500 or less, hydro viscosity or solubility becomes it low that it is 50000 or more dramatically, and handling hydroxyl group content compound.

[0047] (B) As a hydrosilyl group content compound of an ingredient, there is no restriction in particular and various kinds of things can be used, namely, chain polysiloxane  $R^{18}_3SiO[Si(R^{18})_2O]$  — expressed with the general formula 9 or 10 —  $[Si(H)(R^{19})O]_a - b[Si(R^{19})(R^{20})O]_c - SiR^{18}_3$  (9)  
 $a$   $HR^{18}_2SiO[Si(R^{18})_2O]_a - [Si(H)(R^{19})O]_b - [Si(R^{18})(R^{20})O]_c - SiR^{18}_3$  (10)  
 Cyclosiloxane expressed with (an alkyl group of the carbon numbers 1—10 or an aralkyl group, and a show 0 <= a <= 100, b shows 2 <= b <= 100, and c shows [as for R<sup>18</sup> formula , and R<sup>19</sup>] an integer of 0 <= c <= 100, as for an alkyl group of the carbon numbers 1—6 or a phenyl group, and R<sup>20</sup>], and the becomes difficult.

general formula II [00400]  
 [Formula 3]

$$\left[ \begin{array}{c} \text{H} & \text{H} & \text{F}^{22} \\ | & | & | \\ \text{F}^2 & \text{F}^2 & \text{F}^{22} \\ | & | & | \\ (\text{SiO})_4-\text{Si}(\text{O})_5-\text{Si}(\text{O})_5 & & \\ | & | & | \\ \text{F}^{21} & \text{F}^{22} & \text{F}^{22} \\ | & | & | \\ \text{F}^{21} & \text{F}^{22} & \text{F}^{22} \end{array} \right] \quad (11)$$

[0049]R<sup>21</sup> in formula , and R<sup>22</sup> — the alkyl group of the carbon numbers 1-6, or — the alkyl group of

the carbon numbers 1-10 or an aralkyl group, and d show  $0 \leq d \leq 8$ , e shows  $2 \leq e \leq 10$ , and, as for a phenyl group and R<sup>23</sup>, f shows the integer of  $0 \leq f \leq 8$  —  $3 \leq d+f \leq 10$  [ and ] — it is — it can use. Even if it uses these independently and they mix and use two or more sorts, they are not cared about. The chain siloxane which has a phenyl group from a viewpoint of compatibility with an acrylic polymer (meta) and which is shown by the general formulas 12 and 13, and the cyclosiloxane shown by the general formulas 14 and 15 are preferred also in these siloxanes.

$$(CH_3)_3 - 3SiO-[Si(H)(CH_3)O]_2-[Si(C_6H_5)_2O]_2 - Si(CH_3)_3 \quad (12)$$

$$(CH_3)_3 - 3SiO-[Si(H)(CH_3)O]_2-[Si(CH_3)\{CH_2C(H)R^{24}\}_2C_6H_5]_2 - Si(CH_3)_3 \quad (13)$$

(As for hydrogen or a methyl group, and e, in R<sup>24</sup>,  $2 \leq g \leq 100$  and h show a phenyl group among a formula, as for an integer of  $0 \leq h \leq 100$ , and C<sub>6</sub>H<sub>5</sub>)

[0050] [Formula 4]

$$\left[ \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{H} \end{array} \right] - (\text{SiO})_x - (\text{SiO})_y - \boxed{\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{CH}_3 \end{array}} - \left[ \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_5 \end{array} \right] \quad (14)$$

[005] The integer and  $C_6H_5$  as for hydrogen or a methyl group, and whose i,  $2 \leq i \leq 10$  and j are [inside of formula and  $R^1$ ]

(B) As a hardening agent which it has, at least two or more hydroxyl groups of an ingredient further. The compound which makes carry out the addition reaction of the hydroxyl group content compound shown in the formulas 9-15 also after a reaction to the low molecular weight compound which has two or more alketyl groups in a molecule as some hydroxyl groups remain, and is obtained can also be used. As a compound which has two or more alkenyl groups, various

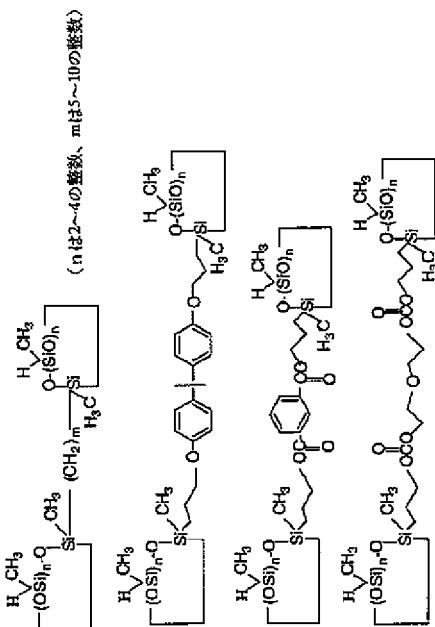
kinds of things can be used into a molecule. If it illustrates, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene. Hydrocarbon system compounds, such as 1,7-octadien, 1,8-nonadiene and 1,9-decadiene. Ether system compounds, such as O,O-dialy bisphenol A and 3,3'-diarylbisphenol A. Carbonate system compounds, such as ester system compounds, such as dialy phthalate, dialy isophthalate, trially trimellitate, and tetraallyl pyromellitate, and diethyleneglycol dialyl carbonate.

[0052] This compound can be obtained by dropping slowly an alkanyl group content compound mentioned to the bottom existence of a hydrosilylation catalyst; and a top to an excessive amount of hydrosilyl group content compounds shown in the formulas 9-15. In consideration of compatibility to the acquisition ease of a raw material, the ease of carrying out of

removal of a siloxane used superfluously, and also a polymer of the (A) ingredient, the following are preferred among such compounds.

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[0054] Although a polymer (A) and a hardening agent (B) are mixable at an arbitrary rate, it is preferred that the mole ratio of an alkanyl group and a hydroxyl group is in the range of 5-0.2 from the field of hardenability, and it is still more preferred that it is especially 2.5-0.4. If smaller [ if a mole ratio becomes five or more, only a hardened material with insufficient hardening and small intensity with stickiness will be obtained, and ] than 0.2, since a hydroxyl group [ activity / in a hardened material / after / hardening ] remains in large quantities, a crack and a void occur, it will be uniform and a hardened material with intensity will not be obtained.

[0055] Although a hardening reaction of a polymer (A) and a hardening agent (B) advances by mixing and heating two ingredients, a hydroxylating catalyst is added in order to advance a reaction more nearly promptly. As such a hydroxylating catalyst, radical initiators, such as organic peroxide and an azo compound, and a transition metal catalyst are mentioned. As a radical initiator, there is no restriction in particular and various kinds of things can be used. If it illustrates, di-t-butylperoxide, 2,5-diethyl- 2,5-JL (t-butylperoxy) hexane, 2,5-dimethyl- 2,5-JL (t-butylperoxy)-3-hexyne. Dialkyl peroxide like dicumyl peroxide, t-butyl cumyl peroxide, alpha, and alpha'-bis(t-butylperoxy) isopropylbenzene. Benzoyl peroxide, p-chlorobenzoyl peroxide, m-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, diarylperoxide like lauroyl peroxide, Peroxy-acid ester like perbenzoic acid-t-butyl, faul-JL diisopropyl carbonates, Peroxylketal like peroxydicarbonate like faul-JL di-carbonate 2-ethylhexyl, 1,1-JL (t-butylperoxy) cyclohexane, and 1,1-JL (t-butylperoxy)-3,3,5-trimethylcyclohexane, etc., are mentioned.

[0056] As a transition metal catalyst, for example A platinum simple substance, alumina, silica, A complex with a thing which made carriers, such as carbon black, distribute a platinum solid, chloroplatinic acid, chloroplatinato acid, alcohol, aldehyde, ketone, etc., a platinum-olefin complex, and a platinum (0)-divinyl tetramethyl disiloxane complex are mentioned. As an example of catalysts other than a platinum compound, RhCl(PPh<sub>3</sub>)<sub>3</sub>, RhCl<sub>3</sub>, RuCl<sub>3</sub>, FeCl<sub>3</sub>, AlCl<sub>3</sub>, PdCl<sub>2</sub>-H<sub>2</sub>O, NiCl<sub>2</sub>, TiCl<sub>4</sub>, etc. are mentioned. These catalysts may be used independently, and even if they use two or more kinds together, they are not cared about. Although there is no restriction in particular as a catalyst, amount, it is good to use in the range of 10<sup>-3</sup> - 10<sup>-6</sup> mol to 1 mol of alkanyl groups of the (A) ingredient often [ using in the range of 10<sup>-1</sup> - 10<sup>-8</sup> mol ], and preferably, if less than 10<sup>-8</sup> mol, hardening will not fully advance. Since a hydroxylating catalyst is expensive, it is preferred that more than 10<sup>-1</sup> mol does not use.

[0057] A uniform hardened material excellent in depths hardenability is obtained without being accompanied by phenomena, such as foaming, if a hydroxylating catalyst is mixed and stiffened [ two ingredients (A), (B), and if needed ]

for this invention. Although there is no restriction in particular about curing conditions, generally it is good to harden [ 0 \*\* - 200 \*\* ] at 30 \*\* - 150 \*\* preferably for 10 seconds - 24 hours. At an elevated temperature (30 \*\* - 150 \*\*), what is hardened in a short time of 10 seconds - about 1 hour is obtained especially. Description of a hardened material can be broadly created from a rubber-like thing to a resin-like thing, although it is dependant on a principal chain skeleton and a molecular weight of a polymer of the (A) ingredient to be used, and a hardening agent of the (B) ingredient. If a concrete use of a hardened material obtained from this constituent is mentioned, they will be a sealing material, adhesives, an adhesive material, elastic adhesives, a paint, powder coatings, foam, a potting material for electric electrons, a film, a gasket, various molding materials, artificial marble, etc.

[0058] An acrylic polymer which has crosslinkable silyl groups at the end of this invention (meta). Like a manufacturing method of an acrylic polymer which has an alkanyl group at the end (meta), An organic halogenated compound or a sulfonyl halide compound An initiator, the 8th fellows of the periodic table, It can obtain by changing halogen of an acrylic polymer which has halogen (meta) into an end which is obtained by a polymerization method using a metal complex which uses nine fellows, ten fellows, or 11 group elements as a central metal and which shows by the general formula 1.

[0059] As such a converting method, an organic halogenated compound or a sulfonyl halide compound An initiator. An acrylic polymer which has terminal structures which show the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements in the general formula 1 with a polymerization method using a metal complex used as a central metal as a catalyst (meta) is manufactured. A method to which a compound having an alkanyl group and crosslinkable silyl groups of polymerization nature is made to react as the 2nd monomer is mentioned. This method is based on the same principle as a method illustrated in a manufacturing method of an acrylic polymer which has an alkanyl group at the end (meta). After the 1st polymerization ends the 2nd monomer and isolating a polymer also in this case, it may add with a catalyst and may be made to newly react, and it may add in the middle of a polymerization (in-situ), and may be made to react. In the case of the latter, a monomer inversion ratio of the 1st polymerization is so good that it is high, and is not less than 80% preferably. Crosslinkable silyl groups will be distributed over a side chain instead of a molecular terminal as it is 80% or less, and the mechanical characteristic of a hardened material will be spoiled. If a compound which has an alkanyl group and crosslinkable silyl groups of such polymerization nature is added in equivalent amount to the number of whole ends, crosslinkable silyl groups will be theoretically introduced into all the ends, but in order to introduce a cross-linking group into a whole and certainly, specifically, it is good to use one to 5 times to the number of ends in excessive amount. If it uses 5 or more times, a cross-linking group will be introduced into an end of a polymer by high density, and it is not desirable on hardened material physical properties.

[0060] Although there is no restriction in particular as a compound which combines and has such an alkanyl group and crosslinkable silyl groups of polymerization nature, if it illustrates concretely, general formula  $\text{R}_2\text{C}-\text{O}(\text{R}')-\text{R}^4-\text{R}^5$  [ Si(R')<sup>2</sup>-YL O ] —  $\text{--S}(\text{R}'\text{Y})$  —  $\text{--S}(\text{R}'\text{Y})$  —  $\text{--S}(\text{R}'\text{Y})$  a (0) (R', R<sup>4</sup>, and R<sup>5</sup> among a formula) R<sup>3</sup> in the general formula 2, R<sup>4</sup>, and R<sup>5</sup> — the same — R<sup>16</sup> and R<sup>17</sup>. All An alkyl group of the carbon numbers 1-20, an aryl group, an aralkyl group, Or (R')<sup>3</sup> SiO — (R' is a univalent hydrocarbon group of the carbon numbers 1-20, and) three R' being the same and differing — \*-\*-\* — when the Tori ORGANO siloxy group shown is shown and R<sup>16</sup> or two or more R<sup>17</sup> exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydroxyl basis and two or more Y exists, they may be the same and may differ, a shows 0, 1, 2, or 3, and b shows 0, 1, or 2, m is an integer of 0-19. However, it shall satisfy that it is a+mb>=1. A compound shown is mentioned. When R<sup>4</sup> is —Cl(O)O— (ester group), it is a compound of an acrylate (meta) system, and when R<sup>4</sup> is a phenylene group, it is a compound of a styrene system.

[0061] Especially as a hydroptic basis shown by the above-mentioned Y, it is not limited, but can use a publicly known thing conventionally, and specifically, A point of hydrogen, a halogen atom, an alkoxy group, an acyloxy group, an KETOKISHI mate group, an amino group, an amide group, an acid-amide group, an aminoxy group, a sulphydryl group, an alkeryoxy group, etc. being mentioned, and hydrolysis nature being mild and being easy to deal with it to especially an alkyloxy group is preferred. This hydroptic basis and a hydroxyl group can be combined with one silicon atom in the 1-3 ranges, and total of atmb, i.e., a hydrolytic basis, has the preferred range of 1-5. When a hydrolytic basis and a hydroxyl group join together in [ two or more ] a reactive silicon group, they may be the same or may differ. The number of silicon atoms which constitute a cross-linking silicon compound may be one, and although they may be two or more pieces, in the case of a silicon atom connected by siloxane bond, there may be about 20 pieces.

formulas, and  $n$ , an integer of 1-20 and  $m$  are the integers of 2-20).  
 $\sigma^- \cdot m^- \cdot p^- H_2 C-OH-C_6 H_4-(CH_2)_n-Si(OCH_3)_3 \cdot Si(CH_3)(OCH_3) \cdot -(CH_2)_n-Si(CH_3) \cdot 2^- \cdot o^- \cdot m^- \cdot p^-$   
 $H_2 C=CH-C_6 H_4-O-(CH_2)_n-Si(OCH_3)_3 \cdot o^- \cdot m^- \cdot p^- H_2 O=C(H-C_6 H_4-O-(CH_2)_n-Si(CH_3)(OCH_3)_2$  (however, inside of

\*\* — it is desirable.

[0063]In a manufacturing method of an acrylic polymer using a metal complex which uses an initiator, the 8th fellows of the periodic table, nine fellows, ten fellows, or 11 group elements as a central metal for an organic halogenated compound or a sulfonyl halide compound as a catalyst (meta), If an organic halogenated compound which has crosslinkable silyl groups is used as an initiator, an acrylic polymer which has crosslinkable silyl groups in one end and in which other ends have the structure of the formula 1 (meta) will be obtained. Thus, if halogen of a stop end of a polymer obtained is

changed into a crosslinkable-silyl-groups content substituent, an acrylic polymer which has crosslinkable silyl groups in both ends (mata) can be obtained. An already indicated method can be used as the converting method.

Although there is no restriction in particular as an organic halogenated compound which has crosslinkable site

groups, what has the structures shown, for example in the general formula 7 is illustrated.  
 $R^1 R^2 C(X)R - i_3 - R^1 I^4 - C(H)(R^1) CH_2 - [Si(R^16)_{2-i_2}(Y_b)O]_m - Si(R^17)_{3-a} Y_a$  (7)  
 (The inside of a formula,  $R^1$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$ ,  $R^{16}$ ,  $R^{17}$ ,  $a$ ,  $b$ ,  $m$ ,  $X$ , and  $Y$  are the same if a compound of the formula 7 is illustrated concretely,  $XCH_2G(O)CH_2Y$ ,  $nSi(OCH_3)_2Si(OCH_3)_3$ ,  $(OCH_3)_3$ ,  $(CH_3)_2C(X)CO$ ,  $O(CH_2)_nSi(OCH_3)_3$ ,  $XCH_2G(O)CH_2$ ,  $nSi(OCH_3)_2Si(OCH_3)_3$ ,  $(CH_3)_2(OCH_3)_2$ ,  $(CH_3)_2COOC(O)O(CH_2)_nSi(CH_3)_3$  ( $OCH_3)_3$  2 in each of above-mentioned

(OCH<sub>3</sub>)<sub>3</sub>; 3'-Omp'-X-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>3</sub>-Si(OCH<sub>3</sub>)<sub>3</sub>; Omp-Cl<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>; Omp'-CH<sub>3</sub>CH<sub>2</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-O-(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub> (in each of above-mentioned formulas, X is chlorine, bromine, or iodine).

\* is mentioned.  
[Q65] What is further the structure shown by the general formula  $\text{C}_n\text{H}_{2n+2}$  as an organic halogenated compound which has

(R<sup>17</sup>)<sub>3-a</sub>(Y)Si-[OSi(R<sup>16</sup>)<sub>2</sub>-B(Y)<sub>b</sub>]<sub>m</sub>-CH<sub>2</sub>-O(H)(R<sup>1</sup>)-R<sup>14</sup>-C(R<sup>11</sup>)(X)-R<sup>15</sup>-R<sup>12</sup> (8)

$\text{2}[\text{CH}_2] \text{ Si}(\text{CH}_3)_3 \text{ C(H)} (\text{X})-\text{CO}_2\text{R}, (\text{CH}_3\text{O})_3 \text{ Si}(\text{CH}_2)_4 \text{ C(H)} (\text{X})-\text{CO}_2\text{R}, (\text{CH}_3)_2\text{C(H)} \text{ Si}(\text{CH}_2)_4 \text{ C(H)}$

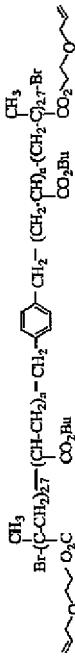
$(CH_2)_3C(H)(X)-O_6H_5$  ( $CH_3O$ )<sub>3</sub> $S(CH_2)_3$  $C(H)(X)-O_6H_5$  ( $CH_3O$ )<sub>2</sub> $(CH_2)Si(CH_3)Si(CH_2)_4C(H)(X)-C_6H_5$  (in each of above-mentioned formulas). As for X, chlorine, bromine or iodine, and R are an alkyl group of the carbon numbers 1–20, an aryl group, and an aralkyl group.

[0065] If an organic halogenated compound which has crosslinkable silyl groups is used as an initiator, a polymer which is halogen end where one end is shown by crosslinkable silyl groups and other ends are shown by the formula 1 will be formed.

obtained, but An acrylic polymer which has crosslinkable silyl groups at the end (meta), can be obtained also by carrying



alpha, and alpha'-dihromo-p-xylene (180 mg), 0.69mmol, the first copper (98 mg, 0.69mmol) of bromination, a 2,2'-bipyridyl (319 g, 2.06mmol) and ethyl acetate (4mL), and acetonitrile (1 mL) were taught, and the sealed tube was carried out, after



[2028]

[Work example 2] In Example 1, the poly(methyl acrylate) which completely has an alkene group in a similar manner in the both ends which have the structure of a lower type was obtained except using methyl acrylate instead of butyl acrylate (93% of yield). In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 7800, and molecular weight distribution was 2.0. The number of the alkene groups introduced per one molecule of oligomer was an average of 3.3 from  $^1\text{H}$  NMR analysis.

[0081]

[Formula 7]

$$\text{CH}_3 \text{Br} - (\text{CH}_2)^7 - (\text{CH} - \text{CH}_2)_n - \text{CH}_2 - \text{C}_6\text{H}_3 - \text{CH}_2 - \text{C}_6\text{H}_3 - \text{CH}_2 - (\text{CH}_2 - \text{CH}_3)_{m-n} - \text{CH}_2 - \text{CH}_3$$

[0082] [Work example 3] To the resisting pressure glass reaction vessel of 50mL, it is butyl acrylate (8.94 g 10 mL), 69.8mmol, alpha, and alpha'-dibromo-p-xylylene (370 mg) 4mmol, the first copper (200 mg, 14mmol) of bromination, a 2,2'-bipyridyl (433 mg, 2.8mmol), and methyl isobutyl ketone (10mL) were taught, and the sealed tube was carried out after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 °C and made to react for 20 minutes. After filtering the insoluble solid which diluted the mixture with ethyl acetate (20mL), and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried  $\text{Na}_2\text{SO}_4$  volatile matter content was distilled off under decompression, and 5.21g of poly (butyl acrylate) which has bromine in both ends was obtained (58%). By GPC measurement (polystyrene conversion), the number average molecular

[0083] Next, the poly (butyl acrylates) (2.0g) produced by the resisting pressure coil of 30mL by performing it above, p-divinylbenzene (281 mg, 2.16mmol), the first copper of bromination (77 mg) 0.54mmol, a 2'-bipyridyl (167 mg, 1.08mmol) and methyl isobutyl ketone (4mL) were taught, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 °C and made to react for 30 minutes. After filtering the insoluble solid which diluted the mixture with ethyl acetate (10mL) and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , volatilized matter content was distilled off under decompression, and 2.11g of poly (butyl acrylates) which has an alkanyl group in the both ends shown in a lower type was obtained. By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 7300, and molecular weight distribution was 2.47. The number of the alkanyl groups

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[0085] [Work example 4] To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (4.47 g 5 mL), 34.9mmol.

alpha, and alpha'-dithromo-p-xylene (180 mg) 0.69mmol), of bromination, a 2,2'-bipyridyl (319 g, 2.06mmol) and ethyl acetate (4mL), and acetonitrile (1 mL) were taught, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 \*\* and made to react for 1 hour. Allyl tributyl tin (0.51mL, 1.64mmol) was added under a nitrogen atmosphere after cooling a mixture, and it was made to react at 100 \*\* for 1 hour. After diluting the mixture with ethyl acetate (20mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrata once by brine twice. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ .

volatile matter content was distilled off under decompression, and the mixture of the polybutyl acrylate which has an alkynyl group in the both ends shown in a lower type, and bromo tributyl tin was obtained [yield of 4.48 g]. In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 7700, and molecular weight distribution was 1.33. The number of the alkynyl groups introduced per one molecule of oligomer was 1.6 from  $\frac{1}{H}$

NMR analysis.  
**[0086]** [Formula 9]

[0087] [Work example 5] To the resisting pressure glass reactor of 30mL, it is methyl acrylate (4.78 g 5 mL), 55.6mmol, alpha, and alpha - dibromo- $\alpha$ -xylene (202 mg) 1.1mmol, the first copper (159 mg, 1.1mmol) of bromination, a 2,2'-bipyridyl (518 mg, 3.3mmol) and ethyl acetate (4mL), and acetonitrile (1mL) were taught, and the sealed tube was carried out, after performing vacuum devolatilization twice and removing dissolved oxygen. The mixture was heated at 130 °\* and made to react for 2.7 hours. After cooling to a room temperature, allyl tributyl tin (0.82mL, 2.68mmol) was added, and it was made to react at 80 °\* for 6 hours. After diluting the mixture with ethyl acetate (20mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , and volatile matter content was distilled off under decompression. The rough product was melted in a small amount of acetone, it reprecipitated twice by hexane, and the poly(methyl acrylate) which has an alketyl group in the both ends shown in a lower type was obtained (yield of 2.80g). In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 7000, and molecular weight distribution was 1.26. The number of the alketyl groups

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$$\text{H} \quad (\text{CH}_2)_n \cdot \text{CH}_2 \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_2 \text{---} (\text{CH}_2)_n$$

[The example 2 of manufacture]

(Manufacturer 1 of the organic halogenated compound which has an alkene group) The nitrogen purge of the two-lot flask of 50mL was carried out, and 2-allyldoxy ethanal (2.5mL, 23.4mmol), pyridine (3mL), and THF (10mL) were taught. The solution was cooled at 0 \*\*\* and 2-bromo propional chloride (2mL, 18.52mmol) was dropped slowly. After continuing churning at a temperature as it is for 1 hour, filtration removed the hydrochloride of the pyridine which added and

brine (10mL) further. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , and volatile matter content was decompression—ization—distilled off. By carrying out distillation under reduced pressure of the obtained rough product, the allyloxy ethyl-2-bromo propionate shown in a lower type was obtained. (78.5–81 \*\* (1.3mmHg), 2.9462).

[0090]  $\text{CH}_3\text{C}(\text{H})(\text{Br})\text{C}(\text{O})\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}$  [0091]

## [The example 3 of manufacture]

(Manufacture 2 of the organic halogenated compound which has an alkanyl group) The nitrogen purge of the two-lot flask of 50mL was carried out, and a 5-hexen-1-ear (2.81mL, 28.4mmol), pyridine (3mL), and THF (10mL) were taught. The solution was cooled at 0 \*\* and 2-bromo propionyl chloride (2mL, 19.52mmol) was dropped slowly. After continuing churning at a temperature as it is for 1 hour, filtration removed the hydrochloride of the pyridine which added and generated ethyl acetate (10mL). Filtrate — dilute hydrochloric acid (10mL) and  $\text{NaHCO}_3$  solution (10mL) — it washed by brine (10mL) further. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , and volatile matter content was decompression—ization—distilled off. By carrying out distillation under reduced pressure of the obtained rough product, the hexenyl-2-bromo propionate shown in a lower type was obtained. (82–83 \*\* (2.3mmHg), 3.101g).

CH<sub>3</sub>C(H)(Br)C(O)-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub> [0092]

[Work example 6] To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (2.5 mL). The initiator which has the alkanyl group obtained in 2.24 g, 17.45mmol, and the example 2 of manufacture (165 mg), 0.698mmol, the first copper (100 mg, 0.680mmol) of bromination, a 2,2'-bipyridyl (2.8 mg, 1.40mmol), acetonitrile (0.5mL), and ethyl acetate (2mL) were prepared, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 \*\* and made to react for 50 minutes. After filtering the insoluble solid which diluted the mixture with ethyl acetate (20mL), and generated it after cooling to a room temperature, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , volatile matter content was distilled off under decompression, and 1.90g of poly (butyl acrylate) which has bromine was obtained in an alkanyl group and other ends to one end (79%). In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 3600, and molecular weight distribution was 1.73.

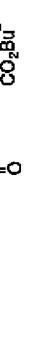
[0093]

[Formula 12]



[0094]

[Formula 13]



[0095]

[Work example 7] To the resisting pressure glass reaction vessel of 30mL, it is methyl acrylate (4.78 g 5 mL), 55.5mmol, 2– (polystyrene conversion), the number average molecular weight of the polymer was 5100, and molecular weight distribution was 1.73.

brine (10mL) further. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , and volatile matter content was decompression—ization—distilled off. By carrying out distillation under reduced pressure of the obtained rough product, the allyloxy ethyl-2-bromo propionate shown in a lower type was obtained. (78.5–81 \*\* (1.3mmHg), 2.9462).

[0096] Next, the polymer (1.17g) produced by 3 mouth flask of 50mL provided with the stirring bar and the flowing-back condenser tube by performing it above,  $\text{Na}_2\text{S}\text{H}_2\text{O}$  (57.6 mg, 0.240mmol), and ethanol (2mL) were taught, and it agitated at flowing-back temperature for 3 hours. After cooling to a room temperature, ethyl acetate (10mL) and dilute hydrochloric acid (10mL) were added, and it separated two-layer. After washing the organic layer by dilute hydrochloric acid and brine and drying by  $\text{Na}_2\text{SO}_4$ , 1.11g of poly(acrylic acid) butyl which has an alkanyl group in the both ends shown in a lower type was obtained by distilling off volatile matter content under decompression. In GPC measurement, by (polystyrene conversion), the number average molecular weight of the polymer was 4200, and molecular weight distribution was 1.71.

[0097]

[Work example 8] To the resisting pressure glass reaction vessel of 100mL, it is butyl acrylate (10 mL). The initiator which has the alkanyl group obtained in 8.94 g, 69.8mmol, and the example 2 of manufacture (332 mg) 1.40mmol, the first copper (200 mg, 1.40mmol) of bromination, a 2,2'-bipyridyl (4.33 mg, 2.80mmol), acetonitrile (2mL), and ethyl acetate (8mL) were prepared, and the sealed tube was carried out, after blowing nitrogen gas for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 \*\* and made to react for 1.5 hours. After cooling to a room temperature, the sealed tube of the p-divinylbenzene (364 mg, 2.80mmol) was added and carried out under a nitrogen gas atmosphere. The mixture was heated at 100 \*\* and made to react for 2 hours. After diluting the mixture with ethyl acetate (30mL) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine twice. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , volatile matter content was distilled off under decompression, and 6.43g of poly(butyl acrylate) which has an alkanyl group in the both ends shown in a lower type was obtained (69%). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 3800, and molecular weight distribution was 5.35. The number of the alkanyl groups introduced per one molecule of oligomer was 1.73 from <sup>1</sup>H NMR analysis.

[0098]

[Work example 9] To the resisting pressure glass reaction vessel of 30mL, it is methyl acrylate (4.78 g 5 mL), 55.5mmol, 2– (polystyrene conversion), the number average molecular weight of the polymer was 5100, and molecular weight distribution was 1.73.

[0099]

[Work example 10] To the resisting pressure glass reaction vessel of 30mL, it is methyl acrylate (4.78 g 5 mL), 55.5mmol, 2– (polystyrene conversion), the number average molecular weight of the polymer was 5100, and molecular weight distribution was 1.73.

[0100]

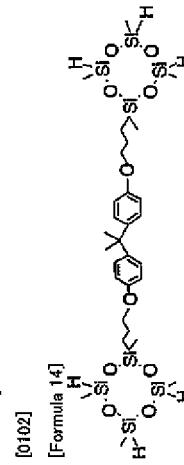
[Work example 11] To the resisting pressure glass reaction vessel of 30mL, it is methyl acrylate (4.78 g 5 mL), 55.5mmol, 2– (polystyrene conversion), the number average molecular weight of the polymer was 5100, and molecular weight distribution was 1.73.

[Work example 12] To the resisting pressure glass reaction vessel of 30mL, it is methyl acrylate (4.78 g 5 mL), 55.5mmol, 2– (polystyrene conversion), the number average molecular weight of the polymer was 5100, and molecular weight distribution was 1.73.

[0100] Examples 9–14] The polymer which has an alkanyl group in the both ends obtained in creation examples 1, 2, 3, 6, 7, and 8 of the hardened material was dissolved in toluene, and a polymer and equivalent weight of steric acid aluminum (the product made from harmony chemicals; KYO word 700PEL) were added. It agitated for 1 hour, and the minute impurities in a polymer were removed. Next, 1, 1 and 3 of the multivalent hydrogen silicon compound shown in a lower type and zerovalent platinum, 3-tetramethyl 1, and 3-divinyl disiloxane complex ( $8.3 \times 10^{-8}$  mol/L xylene solution) were well mixed with the refined poly (acrylic ester). The quantity from which, as for the amount of the multivalent hydrogen silicon compound used, the alkanyl group of a polymer and the hydroxyl group of a hydrogen silicon compound will be 1/1.2 by a mole ratio, and the amount of the platinum catalyst used were made into the  $10^{-4} - 10^{-3}$  equivalent by the mole ratio to the alkanyl group of a polymer.

[0101] Thus, the hardening examination was done on a 130 \*\* hot plate for some obtained constituents, and gel time was measured. It deaerated under decompression of the remaining constituents, heat cure was slushed and carried out to the mold, and the rubber-like hardened material was obtained. The hardened material was immersed in toluene for 24 hours, and the gel fraction was measured from weight changes in front and behind. The result was shown in Table 1.

[0102]



[Table 1]

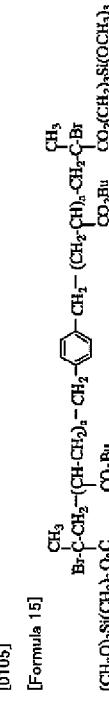
実験例	組合	白金触媒 ( $\times 10^{-4}$ K)	130°C 5分 熱時間	溶化物 重量 (%)	残存物 重量 (%)
実験例 9	室温合 #	1.0 × 1	3 分	1.00℃ 1.0 頃	0 1
実験例 10	室温合 #	1.0 × 1	4.5 分	1.00℃ 1.7 頃	1 5
実験例 11	室温合 #	1.0 × 1	1分40秒	1.00℃ 3.4 頃	7 7
実験例 12	室温合 #	1.0 × 1	4 分	1.00℃ 1.8 頃	7 7
実験例 13	室温合 #	1.0 × 1	2 分	1.00℃ 1.5 頃	4 0
実験例 14	室温合 #	1.0 × 1	1.1 分	1.00℃ 1.2 頃	3 4.

[0104]

[Work example 15] To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (4.47 g 5 mL), 34.9mmol, alpha, and alpha'-dibromo-p-xylene (185 mg), 0.70mmol, the first copper (100 mg, 0.70mmol) of bromination, a 2.2'-bipyridyl (1.09 g, 7.0mmol), and acetonitrile (5mL) were taught, and the sealed tube was carried out, after performing vacuum devolatilization 3 times and removing dissolved oxygen. The mixture was heated at 130 \*\* and made to react for 6 hours. After diluting the mixture with ethyl acetate (ml) and filtering the generated insoluble solid, dilute hydrochloric acid washed filtrate once by brine 3 times. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , volatile matter content was distilled off under decompression, and the poly (butyl acrylate) which has bromine in both ends was obtained (3.04 g, 68% of

polymerization yield). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 6200, and molecular weight distribution was 1.17. Next, the poly (butyl acrylate) (1 g) which has bromine in the both ends obtained by the resisting pressure oil of 30mL in the top, Trimethoxysilylpropyl methacrylate (285 mg, 1.15mmol), When copper (27.6 mg, 0.193mmol), a 2.2'-bipyridyl (300 mg, 1.32mmol), and ethyl acetate (3mL) were prepared for a start [bromination] and it was made to react at 130 \*\* for 6 hours, the poly (butyl acrylate) which has a trimethoxysilyl group at the end shown in a lower type was obtained.

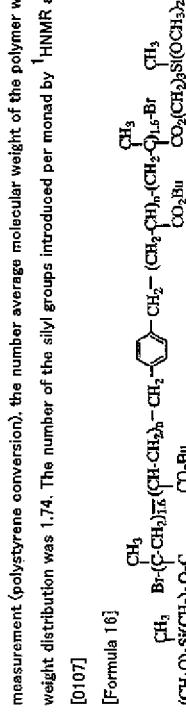
[0105]



[0106]

[Work example 16] To the resisting pressure glass reaction vessel of 30mL, it is butyl acrylate (4.47 g 5 mL), 34.9mmol, alpha, and alpha'-dibromo-p-xylene (185 mg) 0.70mmol, the first copper (100 mg, 0.70mmol) of bromination, a 2.2'-bipyridyl (217 mg, 1.40mmol), ethyl acetate (4mL), and acetonitrile (1mL) were taught, and the sealed tube was carried out, after performing nitrogen bubbling for 10 minutes and removing dissolved oxygen. The mixture was heated at 130 \*\* and made to react for 2 hours. After cooling a mixture, methyl dimethoxy silyl propyl methacrylate (650 mg, 2.8mmol) was added, and it was made to react at 100 \*\* for 2 hours. After diluting with ethyl acetate (20mL) after cooling a mixture and filtering the generated insoluble solid, ammonium chloride solution washed filtrate once by brine twice. The organic layer was dried by  $\text{Na}_2\text{SO}_4$ , volatile matter content was distilled off under decompression, and 4.78g of poly (butyl acrylate) which has a methyl dimethoxy silyl group in the both ends shown in a lower type was obtained (90%). By GPC measurement (polystyrene conversion), the number average molecular weight of the polymer was 7100, and molecular weight distribution was 1.74. The number of the silyl groups introduced per monad by  $^1\text{H}$ NMR analysis was 3.2.

[0107]



[0108] Next, poly (butyl acrylate) (2.5g) and the curing catalyst (Japanese East transformation make, U-220 or 75 mg) which have crosslinkable silyl groups in the both ends produced by performing it above were mixed well, and it shishied into the mold, and deformed at the room temperature using decompression oven. The uniform rubber-like hardened material was obtained by neglecting it for seven days to a room temperature. The gel fraction was 54%.

[0109]

[Effect of the Invention] In this invention, the acrylic (metas) polymer in which manufacturing until now has an alkanyl group or a hydroxylic silyl group by a high ratio at the difficult end can be obtained simple, and those functional groups are certainly introduced into the end. Therefore, the hardened material which was excellent in the hardening characteristic can be obtained. [Translation done.]